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A BINDER-FREE HYDROPHOBIC SILICA ZEOLITE ADSORBENT AND ITS PREPARATION

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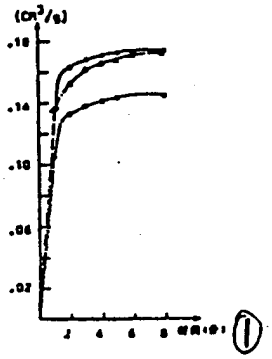
Abstract

The present invention provides a binder-free ZSM-5 hydrophobic silica zeolite adsorbent and the method to prepare it. The method to prepare said adsorbent is: after a powder of ZSM-5 hydrophobic silica zeolite is mixed with a binder containing silicon dioxide and shaped and dried, then in the aqueous solution or vapor of an organic amine or organic quaternary ammonium salt, it is treated under the hydrothermal [sic] conditions, calcined, and it is prepared. In contrast with the binder-containing adsorbents, the adsorbent of the present invention has high adsorbency, fast adsorption rate, and is resistant to high temperature and to corrosion by organic solvents. Therefore, in its application to adsorption separation, some adverse effects caused by the binder can be avoided.



Key: 1 Time (minutes)

Claims

1. An adsorbent, characterized in that it is a binder-free ZSM-5 hydrophobic silica zeolite adsorbent.

2. A method to prepare a binder-free ZSM-5 hydrophobic silica zeolite adsorbent, characterized in that after a powder of ZSM-5 hydrophobic silica zeolite is mixed with a binder containing silicon dioxide and shaped and dried, then in the aqueous solution or vapor of an organic amine or organic quaternary ammonium salt, it is calcined after hydrothermal treatment and is prepared.

3. A method to prepare a binder-free ZSM-5 hydrophobic silica zeolite adsorbent as described in Claim 2, characterized in that the binder containing silicon dioxide is amorphous, such as water glass, white carbon black [sic], silica gel, or a mixture of these.

4. A method to prepare a binder-free ZSM-5 hydrophobic silica zeolite adsorbent as described in Claim 2, characterized in that the organic amine or organic quaternary ammonium salt is:

Alkylamine: $(R)NH_2$, $(R_1R_2)NH$, $(R_1R_2R_3)N$,

Hydroxylmine: ROHNH,

Alkyldiamine: $H_2N(R)NH_2$,

Pyrrolidine: NH [sic],

Quaternary ammonium salt: $(R_1R_2R_3R_4)NOH$,

R_1, R_2, R_3, R_4, and R are alkyl groups of C_1-C_6.

5. A method to prepare a binder-free ZSM-5 hydrophobic silica zeolite adsorbent as described in Claim 2, characterized

in that the temperature for hydrothermal treatment is higher than 100°C, but lower than 220°C.

6. A method to prepare a binder-free ZSM-5 hydrophobic silica zeolite adsorbent as described in Claim 2, characterized in that the temperature for calcination is 300-600°C.

7. A method to prepare a binder-free ZSM-5 hydrophobic silica zeolite adsorbent as described in Claim 2, characterized in that the weight ratio between the ZSM-5 hydrophobic silica zeolite powder and the binder containing silicon dioxide (calculated as SiO_2) is 1:0.11-1.

8. A method to prepare a binder-free ZSM-5 hydrophobic silica zeolite adsorbent as described in Claim 2, characterized in that the product prepared is activated at 600-800°C, by means of steam.

Description

The present invention relates to a solid adsorbent and its preparation, particularly a binder-free ZSM-5 hydrophobic silica zeolite (silicalite-1) adsorbent and its preparation.

As is well known, as a hydrophobic silica zeolite adsorbent, an adhesive must be added to hydrophobic silica zeolite powder to be shaped, to obtain a certain form and strength before it can be applied as an adsorbent. The normal shape can be rods, microspheres, or honeycombs. The inorganic binders used include aluminum oxide, amorphous silicon dioxide such as white carbon black, silica gel, and kaolinite (USP 4,853,355). High polymers such as cellulose acetate and sulfonated divinylbenzene/phenylethylene copolymer can also be used as the binder (USP 4,337,171). The amount of the binder added is

normally 15-20% of the total weight of the adsorbent, and some are even as high as 60%, which indicates a corresponding reduction of the effective adsorption of the zeolite adsorbent. In addition, as the surface properties of the binder are different from the zeolite, when used for adsorption separation, sometimes it may cause adverse effects; while when using a high polymer as a binder, sufficient resistance to high temperature and resistance to corrosion by organic solvent, therefore its range of application is limited.

The purpose of the present invention is to overcome the shortcomings mentioned above, and provide a new hydrophobic silica zeolite adsorbent and the method to prepare it. Said adsorbent has high adsorbency, is resistant to high temperature and corrosion by organic solvent, and when used for adsorption separation, there will not be adverse effects brought about by a binder.

The product of the present invention is a binder-free ZSM-5 hydrophobic silica zeolite adsorbent, which has the following characteristics.

1. X-ray powder diffraction diagram: 2θ is $7.8 \pm 0.1°$, $8.8 \pm 0.1°$, and $23.0 \pm 0.1°$ are the three strongest diffraction peaks (see Figure 1). To detect the 22-25° (2θ) zone using a X-ray slow-scanning technique, the number of diffraction peaks at 23.0°, 23.6°, and 24.5° (2θ) is different due to the difference in symmetry. The number of the diffraction peaks of the ZSM-5 (silicalite-1) of the orthorhombic system at the three angles mentioned above is 2, 2, and 1 respectively (see Figure 2), while that for the monoclinic system is 3, 3, and 2 (see Figure 3).

2. IR absorption spectrum: This is detected through mixed pelleting with KBr; the IR absorption spectrum of the framework

of said adsorbent has the characteristics shown in Figure 4. The optical density ratio between the two absorption peaks at about 550 cm^{-1} and about 450 cm^{-1} in particular is 0.7-0.80. This may also serve as a method to detect the purity of the crystalline phase in the adsorbent of the present invention. When the optical density ratio between the two absorption peaks is 0.8, it indicates that said adsorbent does not contain amorphous silicon dioxide binder and other heterocrystalline phases, that is, the content of ZSM-5 hydrophobic silica zeolite is 100%; and when the optical density ratio between the two absorption peaks is 0.75, it indicates that its content is 95%.

3. For adsorption of n-hexane: the structural porosity of the ZSM-5 hydrophobic silica zeolite is 0.55-0.56 nm, and its theoretical adsorption pore volume is 0.18 cm^3/g. In a vacuum at room temperature (20-25°C), the adsorbent of the present invention was tested using a microelectronic adsorption balance. For the adsorption isotherm of n-hexane vapor (see Figure 5), with the differential pressure $P/p_o = 0.2$, the n-hexane adsorption volume was greater than 0.171 cm^3/g (equivalent to 112.5 mg/g), indicating that the content of ZSM-5 hydrophobic silica zeolite in the adsorbent of the present invention is greater than 95%.

4. Rate of adsorption: In a vacuum at room temperature (20-25°C), the rate of adsorption of the adsorbent of the present invention when the pressure of n-hexane vapor [sic] is 2 torr was tested using a microelectronic adsorption balance. It was apparently higher than that of the adsorbent in which the silicon dioxide binder has not been converted to ZSM-5 hydrophobic silica zeolite (See Figure 6).

5. Hydrophobic adsorption: Hydroscopicity of the adsorbent of the present invention at the room temperature was tested using the same method for testing the adsorption isotherm of n-hexane. Water adsorption volume when $P/p_o=0.3$ was used for comparison. The adsorption volume of the adsorbent of the present invention of water is less than the adsorption volume of n-hexane, that is, it is hydrophobic.

The method of preparing a binder-free ZSM-5 hydrophobic silica zeolite adsorbent of the present invention is: after the ZSM-5 hydrophobic silica zeolite powder (also known as silicalite-1) and a binder containing silicon dioxide are mixed and shaped (into rods, microspheres, or honeycombs) and dried, it is put into a sealed reactor, and then in the aqueous solution or vapor of an organic amine or organic quaternary ammonium salt, it undergoes hydrothermal treatment before calcination, and the adsorbent of the present invention is prepared. After hydrothermal treatment, the binder containing silicon dioxide is basically converted to ZSM-5 hydrophobic silica zeolite. The effect of calcination is to remove organic substances in the adsorbent, otherwise they will block the pores of the adsorbent. The adsorbent of the present invention prepared using the above method has a content of ZSM-5 hydrophobic silica zeolite (weight percentage, the same hereafter) greater than 95%, and adsorption of water (weight percentage, the same hereafter) 5-7%. The X-ray powder diffraction analysis shows that the structure of the adsorbent is orthorhombic. If the adsorbent prepared using the above method is activated with steam at 600-800°C, its hydrophobicity may be even better, and its adsorption of water is about 1% or so. By means of the X-ray powder diffraction, it is determined if the structure of the adsorbent is monocrystalline.

The time of activation with steam mentioned above is normally 4-48 h; at a high temperature, the time of activation may be shorter; while at a lower temperature, the time of activation may be longer.

The silicon-dioxide-containing binder used in the present invention is amorphous, such as white carbon black, water glass, silica gel, or a mixture of these. When water glass is used as the binder, acid must be added to neutralize the alkalinity before use. The acid used may be sulfuric acid, hydrochloric acid, etc.

The ratio in weight between the ZSM-5 hydrophobic silica zeolite powder and the silicon-dioxide-containing binder used in the present invention (calculated as SiO_2) is 1:0.11-1. When white carbon black is used as the binder or when the amount of the liquid binder added is small, water must be added. The amount of water added should be such that the binder and the powder can be mixed, kneaded, and shaped.

The organic amine or organic quaternary ammonium salt used in the present invention are as follows.

Alkyl amine: $(R)NH_2$, $(R_1R_2)NH$, $(R_1R_2R_3)N$,

Hydroxylmine: ROHNH,

Alkyldiamine: $H_2N(R)NH_2$,

Pyrrolidine: NH,

Quaternary ammonium salt: $(R_1R_2R_3R_4)NOH$,

R_1, R_2, R_3, R_4, R are alkyl groups of C_1-C_6.

The temperature of the hydrothermal treatment for the present invention is higher than 100°C, but lower than 220°C. When the temperature is lower, the time for the hydrothermal treatment is longer; while when the temperature is higher, the time for the hydrothermal treatment may be shorter. In general,

the goal is to ensure the silicon dioxide in the binder is basically converted to silica zeolite, that is, to guarantee that the content of the ZSM-5 hydrophobic silica zeolite of the present invention is higher than 95%. The calcination temperature after the hydrothermal treatment is 300-600°C, and the calcination time is normally 2-10 h.

The binder-free ZSM-5 hydrophobic silica zeolite adsorbent of the present invention, in contrast with the binder-containing ones, has the following obvious advantages: high adsorbency, fast adsorption rate, resistance to high temperature and resistance to corrosion by organic solvents, and when used for adsorption separation, it has the ability to avoid some of the adverse effects caused by a binder.

Attached drawings. Figure 1 is the X-ray powder diffraction diagram of the adsorbent of the present invention. Figure 2 is the X-ray powder diffraction slow-scanning diagram of the adsorbent orthorhombic system of the present invention (22-25°C/2θ). Figure 3 is the X-ray powder diffraction slow-scanning diagram of the adsorbent monocrystalline system of the present invention (22-25°C/2θ). Figure 4 is the IR absorption spectrum of the adsorbent of the present invention. Figure 5 is the the diagram of the isotherm of the n-hexane vapor adsorption (25°C). ● is the adsorption isotherm of the ZSM-5 hydrophobic silica zeolite adsorbent that contains SiO_2 binder that has not been converted; Δ is the adsorption isotherm of the ZSM-5 hydrophobic silica zeolite powder; O is the adsorption isotherm of the adsorbent of the present invention. Figure 6 is the n-hexane adsorption rate curve (25°C), in which ● is the adsorption rate curve of the ZSM-5 hydrophobic silica zeolite adsorbent that contains SiO_2 binder that has not been converted; Δ is the

adsorption rate curve of the ZSM-5 hydrophobic silica zeolite powder; O is the adsorption rate curve of the adsorbent of the present invention.

Examples.

Example 1: After 80 g ZSM-5 hydrophobic silica zeolite powder (hereafter "powder") and 80 g white carbon black, are mixed with water and kneaded, shaped, and dried, it is placed into a reactor and sealed. After hydrothermal treatment at 160°C, it is calcined at 600°C in the solution of 40% tetrapropyl ammonium hydroxide. It is determined that the content of the ZSM-5 hydrophobic silica zeolite in the adsorbent prepared is higher than 95%, and its adsorption of water is 6%. After the adsorbent is activated with steam at 800°C, the adsorption of water is less than 1%.

Example 2: After 80 g powder and 134 g water glass are mixed, shaped, and dried, it is placed into a reactor and sealed. After hydrothermal treatment at 200°C, it is calcined at 400°C inethylamine vapor. It is determined that the content of the ZSM-5 hydrophobic silica zeolite in the adsorbent prepared is higher than 95%, and its adsorption of water is 7%. After the adsorbent is activated with steam at 700°C, the adsorption of water is less than 1%.

Before water glass (content of SiO_2 is 30%) is mixed with the powder, its alkalinity is first neutralized with 6N sulfuric acid.

Example 3: After 80 g powder and 30 g silica gel (content of SiO_2 is 30%) are mixed, shaped, and dried, it is placed in a reactor and sealed. After hydrothermal treatment at 105°C, it is

calcined at 380°C in ethylamine vapor. It is determined that the content of the ZSM-5 hydrophobic silica zeolite in the adsorbent prepared is higher than 95%, and its adsorption of water is 6.5%. After the adsorbent is activated with steam at 600°C, the adsorption of water is less than 1%.

Example 4: After 80 g powder, 10 g white carbon black, and 33 g silica gel (containing SiO_2 30%) are mixed with water, shaped, and dried, [the mixture] is placed into a reactor and sealed. After hydrothermal treatment at 220°C, it is calcined at 500°C in a solution of pyrrolidine. It is determined that the content of the ZSM-5 hydrophobic silica zeolite in the adsorbent prepared is higher than 95%, and its adsorption of water is 7%. After the adsorbent is activated with steam at 680°C, the adsorption of water is less than 1%.

Drawings Attached to the Description

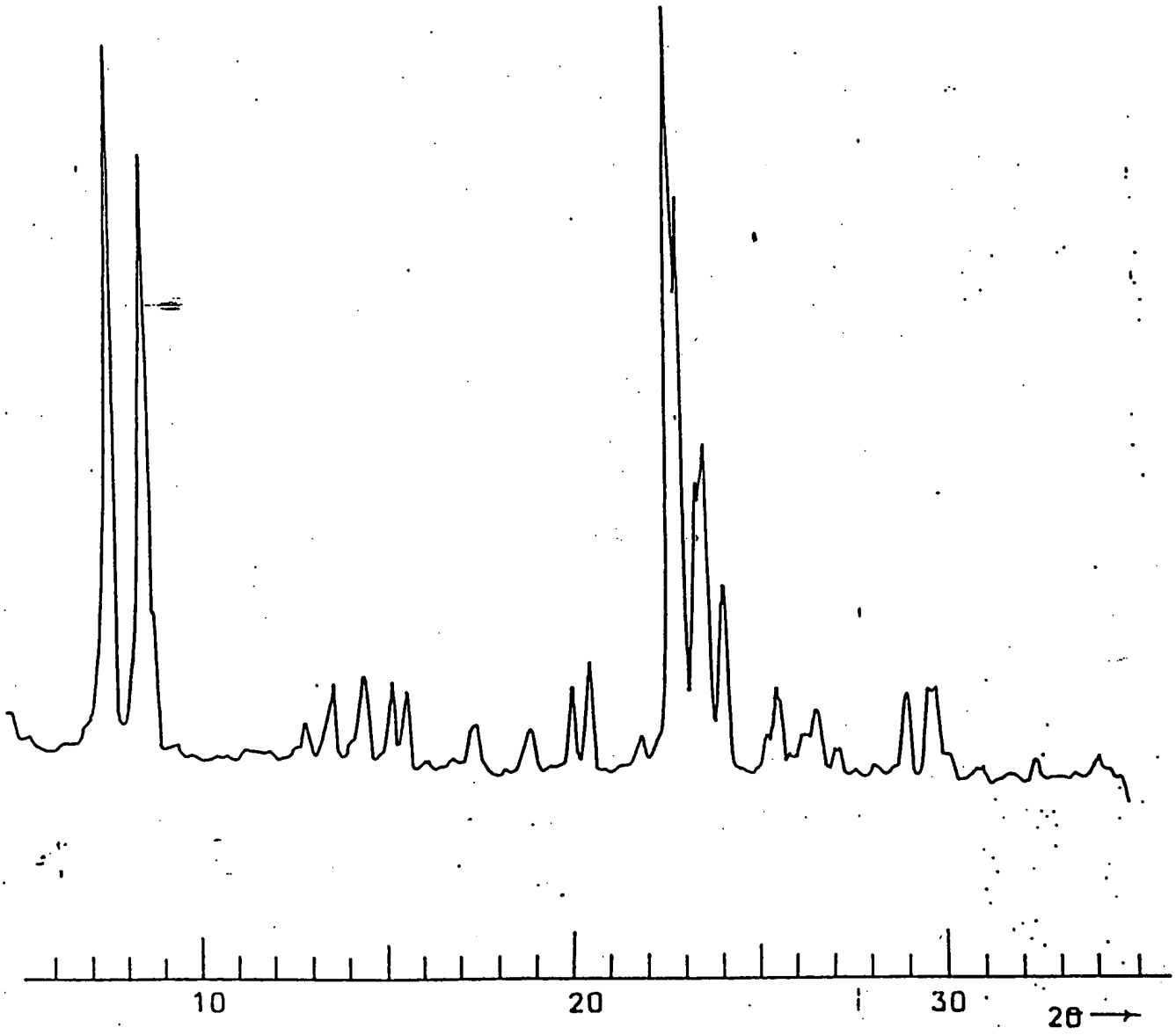


Figure 1

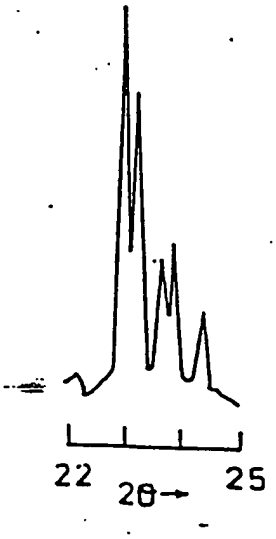


Figure 2

Figure 3

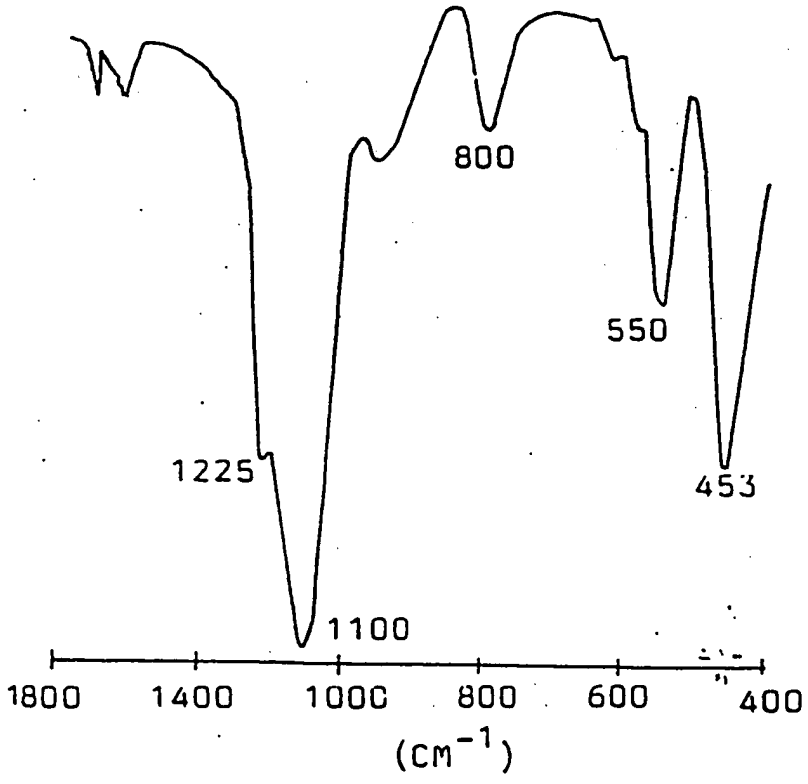


Figure 4

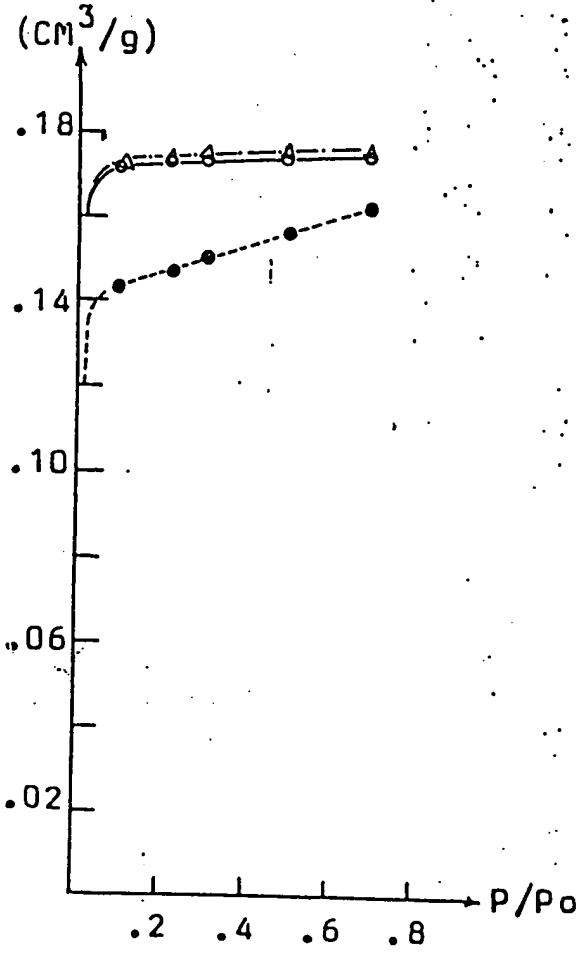


Figure 5

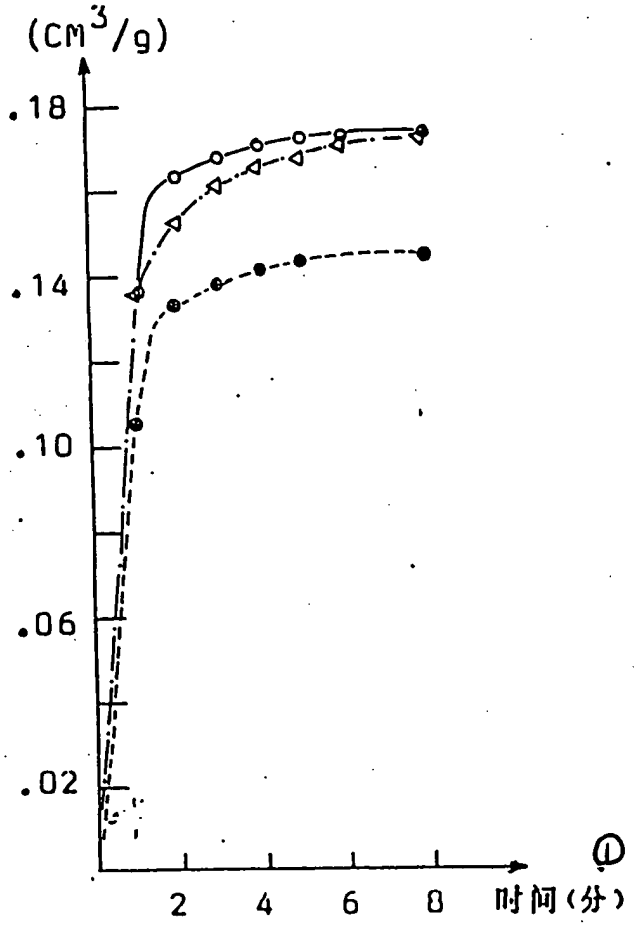


Figure 6

Key: 1 Time (minute)